Supporting Information

One-Pot Four-Component Reaction: Aqueous $\text{TiCl}_3/\text{PhN}_2^+$ Mediated Alkyl Radical Addition to Imines Generated *in Situ*

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General

All reactions were performed under N_2 . Melting points are uncorrected. ^1H and ^{13}C NMR were recorded at 250 and 62.8 Mz, respectively. Benzaldehyde, *p*-tolualdehyde and aniline were distilled prior use. The aqueous acidic 15% TiCl_3 solution was purchased from C. Erba. Flash column chromatography was performed by using 40-63 μm silica gel packing.

Typical procedure for the alkyl radical addition. Method I: After optimization (entry 7 of table 1 and entries 4,6 of Table 2), the best procedure was as follows. To a glacial CH_3COOH solution (15 mL), at 20°C , containing 2.5 mmol of aldehyde **1a-c**, 3.75 mmol of amine **2a-c**, 7.5 mmol of R-I (2.5 mmol in case of benzyl iodide, entry 11 of Table 1) and 6.5 mmol of TiCl_3 (ca. 7 mL of a commercially solution) was added portionwise, over 2 h. under stirring, the phenyldiazonium fluoborate (3.75 mmol). After being stirred, at the same temperature, for additional 20 min., the reaction mixture was extracted with EtOAc (4x50 mL). The combined organic phase was washed (2x15 mL of H_2O), dried over anhydrous Na_2SO_4 and concentrated at reduced pressure in order to eliminate most of CH_3COOH and unreacted R-I. ^1H NMR of the crude mixture revealed that the alkylated products **4** were extracted in their protonated form. The resulting crude residue was dissolved in EtOAc (50 mL), cooled in an ice-bath and added with an aqueous 10% NaOH solution until basic pH. The aqueous phase was then extracted two times with EtOAc. The combined organic layers, upon remaining work-up (H_2O , Na_2SO_4 , concentration *in vacuo*), were successively purified by flash column chromatography (EtOAc/hexane, 9:1) affording **4**, usually as a yellow oil. **Method II:** a cold solution of benzenediazonium chloride, obtained by diazotation of aniline (3.75 mmol in 2 mL of 50% HCl) with a solution of NaNO_2 (3.9 mmol in 6 mL of H_2O) was added dropwise over 2 h. to the solution described in Method I. Successive work-up was as for Method I.

Spectroscopic data.

N-(4-Methoxyphenyl)-{1-(*p*-bromophenyl)-ethyl}amine (4a**).^a Purification by flash column chromatography (hexane/EtOAc, 9:1) gave **4a** (420 mg, 55%, Table 1, entry 2) as a pale yellow oil. ^1H NMR (DMSO) δ (ppm) 1.37 (3H, CH_3 , d, $J = 6.5$ Hz), 3.57 (3H, OCH_3 , s), 4.0 (1H, NH, s br, D_2O exchangeable), 4.37 (1H, CH, q, $J = 6.5$ Hz), 6.42 (2H, Ar'H, d, $J = 8.7$ Hz), 6.61 (2H, Ar'H, d, $J = 8.7$ Hz), 7.31 (2H, Ar H, d, $J = 8.7$ Hz), 7.46 (2H, Ar H, d, $J = 8.7$ Hz). ^{13}C NMR (CDCl_3) δ 25. (CH_3), 53.9 (CH), 55.9 (OCH_3), 114. (2CH), 114.9 (CH), 120.5(C), 128.0 (CH), 131.9 (CH), 141.4(C), 144.9 (C), 152.2 (C) ppm. MS (EI, 70 eV) m/z 307-305 (M^+ , 50), 292-290 ($\text{M}-\text{CH}_3$, 100). HMRS calcd for $\text{C}_{15}\text{H}_{16}\text{BrNO}$: 305.0415; found 305.0416. Anal. calcd for $\text{C}_{15}\text{H}_{16}\text{BrNO}$: C, 58.84; H, 5.27; N, 4.57. Found 58.79, 5.25, 4.56. ^aChi, J.; Zhou, Y-G.; Zhang, X.; *J. Org. Chem.* **2003**, 68, 4120-4122.**

N-(4-Methoxyphenyl)-{1-(*p*-bromophenyl)-octyl}amine (4b**). Purification by flash column chromatography (hexane/EtOAc, 95:5) of the crude material gave **4b** (700 mg, 72%, Table 1, entry 4) as a yellow oil. ^1H NMR (CDCl_3) δ (ppm) 0.86 (3H, CH_3 , t, $J = 7.0$ Hz), 1.2-1.35 (10H, 5 CH_2 , m), 1.7 (2H, CH_2 , m), 3.4 (1H, NH, s br, D_2O exchangeable), 3.68 (3H, OCH_3 , s), 4.16 (1H, CH, t, J**

= 6.5 Hz), 6.42 (2H, Ar'H, d, J = 9.0 Hz), 6.67 (2H, Ar'H, d, J = 9.0 Hz), 7.20 (2H, Ar H, d, J = 8.5 Hz), 7.41 (2H, Ar H, d, J = 8.5 Hz). MS (EI, 70 eV) m/z 391-389 (M, 30), 292-290 (M-heptyl, 100). ^{13}C NMR (CDCl_3) δ 14.0 (CH_3), 22.5 (CH_2), 26.2 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 31.7 (CH_2), 38.9 (CH_2), 55.7 (CH-NH), 58.5 (OCH_3), 114.5 (CH), 114.7 (CH), 120.3 (CH), 128.2 (CH), 131.5 (CH), 141.3 (C), 143.6 (C), 151.9 (C) ppm. HMRS calcd for $\text{C}_{21}\text{H}_{28}\text{BrNO}$: 389.1354; found 389.1356.

N-(4-Methoxyphenyl)-{1-(*p*-bromophenyl)-2-methyl-propyl}amine (4c). Purification by flash column chromatography (hexane/EtOAc, 95:5) afforded **4c** (634 mg, 76%, Table 1, entry 7) as a yellow orange oil. ^1H NMR (DMSO) δ (ppm) 0.77 (3H, CH_3 , d, J = 6.7 Hz), 0.98 (3H, CH_3 , d, J = 6.7 Hz), 1.92 (1H, CH, octet, J = 6.7 Hz), 3.56 (3H, OCH_3 , s), 3.99 (1H, CH, t, J = 7.9 Hz, d after D_2O exchange), 5.58 (1H, NH, d, J = 7.9 Hz, D_2O exchangeable), 6.46 (2H, Ar'H, d, J = 8.9 Hz), 6.59 (2H, Ar'H, d, J = 8.9 Hz), 7.28 (2H, Ar H, d, J = 8.4 Hz), 7.44 (2H, Ar H, d, J = 8.4 Hz). ^{13}C NMR (CDCl_3) δ 18.6 (CH_3), 19.5 (CH_3), 34.7 (CH), 55.7 (OCH_3), 64.4 (CH-NH), 114.7 (CH), 120.5 (CH), 127.8 (C), 129.1 (CH), 131.3 (CH), 141.2 (C), 141.6 (C), 152.1 (C) ppm. MS (EI, 70 eV) m/z 335-333 (M^+ , 25), 292-290 (M - *i*-Pr, 100). HMRS calcd for $\text{C}_{17}\text{H}_{20}\text{BrNO}$: 333.0728; found 333.0727.

N-(4-Methoxyphenyl)-{1-(*p*-bromophenyl)-1-*c*-hexyl-methyl}amine (4d). Purification by flash column chromatography (hexane/EtOAc, 9:1) gave **4d** (560 mg, 60%, Table 1, entry 8) as a yellow orange oil. ^1H NMR (DMSO) δ (ppm) 0.8-1.8 (10H, 5CH_2 , m), 1.96 (1H, CH, m), 3.56 (3H, OCH_3 , s), 4.01 (1H, CH, t, J = 7.7 Hz, d after D_2O exchange), 5.61 (1H, NH, d, J = 7.7 Hz, D_2O exchangeable), 6.45 (2H, Ar'H, d, J = 8.9 Hz), 6.58 (2H, Ar'H, d, J = 8.9 Hz), 7.26 (2H, Ar H, d, J = 8.3 Hz), 7.43 (2H, Ar H, d, J = 8.3 Hz). ^{13}C NMR (DMSO) δ 25.6 (CH_2), 25.8 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 43.4 (CH), 55.1 (OCH_3), 62.0 (CH-N), 114.2 (CH), 119 (CH), 129.4 (CH), 130.5 (CH), 131.3 (C), 132.1 (C), 142.2 (C), 150.3 (C) ppm. MS (EI, 70 eV) m/z 375-373 (M^+ , 20), 292-290 (M - *c*-hexyl, 100). HMRS calcd for $\text{C}_{20}\text{H}_{24}\text{BrNO}$: 373.1041; found 373.1039.

N-(4-Methoxyphenyl)-{1-(*p*-bromophenyl)-2-phenyl-ethyl}amine (4e). The reaction was performed by using equimolar amount of 4-Br-benzaldehyde and benzyl iodide. Purification of the crude residue by flash column chromatography (hexane/EtOAc, 9:1) afforded **4e** as a thick colourless oil (735 mg, 77%, Table 1, entry 11). ^1H NMR (CDCl_3) δ (ppm) 2.96 (1H, CH_2 , dd, J = 13.8, 8.0 Hz), 3.06 (1H, CH_2 , dd, J = 13.8, 5.8 Hz), 3.66 (3H, OCH_3 , s), 4.45 (1H, CH, dd, J = 8.0, 5.8 Hz), 6.37 (2H, Ar'H, d, J = 8.7 Hz), 6.64 (2H, Ar'H, d, J = 8.7 Hz), 7.10 (2H, Ph H, m), 7.18 (2H, Ar H, d, J = 8.0 Hz), 7.24 (3H, Ph H, m), 7.40 (2H, Ar H, d, J = 8.0 Hz). ^{13}C NMR (CDCl_3) δ 44.8 (CH_2), 55.6 (OCH_3), 60.0 (CH-N), 114.6 (CH), 115.4 (CH), 120.8 (C-Br), 126.8 (CH), 128.4 (CH), 128.6 (CH), 129.2 (CH), 131.6 (CH), 137.1 (C), 140.3 (C), 142.2 (C), 152.6 (C) ppm. MS (EI, 70 eV) m/z 383-381 (M^+ , 15), 292-290 (M - PhCH_2 , 80), 91 (100). HMRS calcd for $\text{C}_{21}\text{H}_{20}\text{BrNO}$: 381.0729; found 381.0731.

N-Benzyl-N-(4-methoxyphenyl)-{1-(*p*-bromophenyl)-2-phenyl-ethyl}amine iodide salt (4ee salt). The reaction was performed by using a molar ratio 4-Br-benzaldehyde/benzyl iodide of 1:3 (Table 1, entry 12). By extracting the aqueous acidic solution with EtOAc, **4ee** was obtained as a iodide salt (1.27 g, 85%). Yellow solid, mp 120-5 °C (from EtOAc). ^1H NMR (CD_3COCD_3) δ (ppm) 3.51 (1H, CH_2 -C, dd, J = 13.5, 11.1 Hz), 3.68 (1H, CH_2 -C, dd, J = 13.5, 4.9 Hz), 3.75 (3H, OCH_3 , s), 4.69 (1H, CH_2 -N, d, J = 13.5 Hz), 4.97 (1H, CH_2 -N, d, J = 13.5 Hz), 5.53 (1H, CH, dd, J = 11.1, 4.9 Hz), 6.90 (2H, Ar'H, d, J = 9.2 Hz), 7.15 (5H, Ph H, s), 7.23 (3H, Ph H, m), 7.30 (2H, Ph H, m), 7.51 (2H, Ar H, d, J = 8.0 Hz), 7.55 (2H, Ar'H, d, J = 9.2 Hz), 7.62 (2H, Ar H, d, J = 8.0 Hz). MS (EI, 70 eV) m/z 473-471 (M^+ , 10), 382-380 (M - PhCH_2 , 40), 292-290 (60), 91 (100).

N-Benzyl-N-(4-methoxyphenyl)-{1-(*p*-bromophenyl)-2-phenyl-ethyl}amine (4ee). The salt of **4ee** was taken up in 150 mL of EtOAc and added with an aqueous 10% NaOH solution until basic pH. The organic layer, upon remaining work up (Na₂SO₄, concentration in vacuo), afforded pure **4ee** as white solid: mp 95-8 °C (from MeOH/Et₂O). ¹H NMR (CDCl₃) δ (ppm) 3.08 (1H, CH₂-C, dd, J = 13.9, 8.3 Hz), 3.32 (1H, CH₂-C, dd, J = 13.9, 6.6 Hz), 3.71 (3H, OCH₃, s), 4.05 (1H, CH₂-N, d, J = 15.5 Hz), 4.32 (1H, CH₂-N, d, J = 15.5 Hz), 4.86 (1H, CH, dd, J = 8.3, 6.6 Hz), 6.71 (4H, Ar'H, AB system, J = 9.4 Hz), 7.10-7.21 (12H, 2Ph H + 2Ar H, m), 7.37 (2H, Ar H, d, J = 8.3 Hz). MS (CI) *m/z* 473-471 (M⁺, 10), 382-380 (M – PhCH₂, 100). HMRS calcd for C₂₈H₂₆NOBr: 471.1198; found 471.1196.

N-(4-Methoxyphenyl)-{1-phenyl-2-methyl-propyl}amine (4f). Purification by flash column chromatography (hexane/EtOAc, 9:1) gave **4f** (383 mg, 60%, Table 2, entry 1) as a yellow orange oil. ¹H NMR (CDCl₃) δ (ppm) 0.90 (3H, CH₃, d, J = 6.7 Hz), 0.97 (3H, CH₃, d, J = 6.7 Hz), 2.01 (1H, CH, octet, J = 6.7 Hz), 3.66 (3H, OCH₃, s), 4.03 (1H, CH, d, J = 6.7 Hz), 6.44 (2H, Ar'H, d, J = 9.0 Hz), 6.65 (2H, Ar'H, d, J = 9.0 Hz), 7.2-7.3 (5H, Ph H, m). ¹³C NMR (CDCl₃) δ 18.7 (CH₃), 19.6 (CH₃), 34.8 (CH), 55.7 (OCH₃), 65.1 (CH-N), 114.6 (CH), 114.8 (CH), 126.8 (CH), 127.3 (CH), 128.1 (CH), 141.3 (C), 142.3 (C), 152.0 (C-O) ppm. MS (EI, 70 eV) *m/z* 255 (M⁺, 10), 212 (M – *i*-Pr, 100). HMRS calcd for C₁₇H₂₁NO: 255.1623; found 255.1622.

N-(4-Methoxyphenyl)-{1-(*p*-tolyl)-2-methyl-propyl}amine (4g). Purification by flash column chromatography (hexane/EtOAc, 95:5) gave **4g** (470 mg, 70%, Table 2, entry 4) as an orange oil. ¹H NMR (CDCl₃) δ (ppm) 0.96 (3H, CH₃, d, J = 6.7 Hz), 1.03 (3H, CH₃, d, J = 6.7 Hz), 2.05 (1H, CH, octet, J = 6.7 Hz), 2.37 (3H, CH₃, s), 2.4 (1H, NH, br, D₂O exchangeable), 3.73 (3H, OCH₃, s), 4.08 (1H, CH, d, J = 6.7 Hz), 6.52 (2H, Ar'H, d, J = 8.9 Hz), 6.73 (2H, Ar'H, d, J = 8.9 Hz), 7.15 (2H, Ar H, d, J = 8.2 Hz), 7.23 (2H, Ar H, d, J = 8.2 Hz). ¹³C NMR (CDCl₃) δ 18.8 (CH₃), 19.6 (CH₃), 21.0 (CH₃), 34.8 (CH), 55.7 (OCH₃), 64.6 (CH-N), 114.6 (CH), 114.8 (CH), 127.2 (CH), 128.6 (C-Br), 128.8 (CH), 139.6 (C), 141.9 (C), 151.9 (C-O) ppm. MS (EI, 70 eV) *m/z* 269 (M⁺, 10), 226 (M – *i*-Pr, 100). HMRS calcd for C₁₈H₂₃NO: 269.1779; found 269.1780.

N-(*p*-Tolyl)-{1-(*p*-bromophenyl)-2-methyl-propyl}amine (4h). Purification by flash column chromatography (hexane/EtOAc, 9:1) afforded **4h** (556 mg, 70%, Table 2, entry 6) as a reddish oil. ¹H NMR (CDCl₃) δ (ppm) 0.89 (3H, CH₃, d, J = 6.6 Hz), 0.95 (3H, CH₃, d, J = 6.6 Hz), 1.98 (1H, CH, octet, J = 6.6 Hz), 2.15 (3H, CH₃, s), 4.03 (1H, CH, d, J = 6.6 Hz), 6.38 (2H, Ar'H, d, J = 8.3 Hz), 6.86 (2H, Ar'H, d, J = 8.3 Hz), 7.15 (2H, Ar H, d, J = 8.3 Hz), 7.38 (2H, Ar H, d, J = 8.3 Hz). ¹³C NMR (CDCl₃) δ 18.5 (CH₃), 19.5 (CH₃), 20.3 (CH₃), 34.7 (CH), 63.8 (CH-N), 113.6 (CH), 129.0 (CH), 129.6 (CH), 129.8 (C-Br), 130.0 (C), 131.3 (CH), 136.1 (C), 148.8 (C-N) ppm. MS (EI, 70 eV) *m/z* 319-317 (M⁺, 15), 276-274 (M – *i*-Pr, 100), 91 (30). HMRS calcd for C₁₇H₂₀BrN: 317.0779; found 317.0777.

N-Phenyl-{1-(*p*-bromophenyl)-2-methyl-propyl}amine (4i). Purification by flash column chromatography (hexane/EtOAc, 85:15) afforded **4i** (342 mg, 45%, Table 3, entry 1) as a reddish oil (first eluted product). ¹H NMR (CDCl₃) δ (ppm) 0.91 (3H, CH₃, d, J = 7.0 Hz), 0.98 (3H, CH₃, d, J = 6.5 Hz), 2.05 (1H, CH, m), 4.08 (1H, CH, d, J = 6.0 Hz), 6.51 (2H, Ph H, d, J = 7.5 Hz), 6.66 (1H, Ph H, t, J = 7.53 Hz), 7.07 (2H, Ph H, t, J = 7.5 Hz), 7.18 (2H, Ar H, d, J = 8.5 Hz), 7.41 (2H, Ar H, d, J = 8.5 Hz). ¹³C NMR (CDCl₃) δ 18.5 (CH₃), 19.5 (CH₃), 34.7 (CH), 63.6 (CH-N), 113.5 (CH), 117.6 (CH), 120.5 (C-Br), 129.0 (CH), 129.1 (CH), 131.3 (CH), 141.5 (C), 147.1 (C) ppm. MS (EI, 70 eV) *m/z* 305-303 (M⁺, 10), 262-260 (M – *i*-Pr, 100). HMRS calcd for C₁₆H₁₈BrNO: 303.0623; found 303.0622. The second eluted product was the **Triarylmethane derivative (5i)** (116 mg, 6% molar yield) as a green oil. ¹H NMR (DMSO) δ (ppm) 0.75 (6H, 2CH₃, d, J = 6.54 Hz), 1.05 (6H, 2CH₃, d, J = 6.54 Hz), 1.91 (2H, 2CH, octet, J = 6.54 Hz), 3.97 (2H, 2CH-N, t, J =

7.85 Hz, d after D₂O exchange), 5.05 (1H, CH, s), 6.01 (1H, NH, d, J = 7.85 Hz), 6.41 (4H, Ar'H, d, J = 8.7 Hz), 6.62 (4H, Ar'H, d, J = 8.7 Hz), 6.92 (2H, Ar H, d, J = 8.3 Hz), 7.27 (4H, Ar H, d, J = 8.28 Hz), 7.37 (2H, Ar H, d, J = 8.3 Hz), 7.44 (4H, Ar H, d, J = 8.28 Hz). MS (CI) m/z 778-776-774-772 (M^+ , Br₃ pattern, 100). HMRS calcd for C₃₉H₃₉N₂Br₃: 772.0663; found 772.0665.

N-Phenyl-{2-methyl-1-*p*-tolyl-propyl}amine (4j). Purification by flash column chromatography (hexane/EtOAc, 85:15) afforded **4j** (280 mg, 47%, Table 3, entry 2) as a reddish oil (first eluted product). ¹H NMR (CDCl₃) δ (ppm) 0.90 (3H, CH₃, d, J = 6.9 Hz), 0.97 (3H, CH₃, d, J = 6.9 Hz), 2.01 (1H, CH, octet, J = 6.9 Hz), 2.29 (3H, CH₃, s), 4.08 (1H, CH, d, J = 6.9 Hz), 4.3 (1H, NH, s br, D₂O exchangeable), 6.50 (2H, Ar'H, d, J = 7.9 Hz), 6.60 (1H, Ar'H, t, J = 6.9 Hz), 7.0-7.20 (6H, 2Ar'H + 4Ar H, m). ¹³C NMR (CDCl₃) δ 18.7 (CH₃), 19.6 (CH₃), 21.0 (CH₃), 34.7 (CH), 63.8 (CH-N), 113.4 (CH), 113.5 (CH), 117.2 (CH), 127.1 (CH), 128.8 (CH), 129.0 (CH), 136.2 (C), 139.1 (C), 147.3 (C-N) ppm. MS (EI, 70 eV) m/z 239 (M^+ , 15), 196 ($M - i$ -Pr, 100). HMRS calcd for C₁₇H₂₁N: 239.16739; found 239.1674. The second eluted product was the **Triarylmethane derivative (5j)** (72.5 mg, 5% molar yield) as a green oil. ¹H NMR (CDCl₃) δ (ppm) 0.85 (6H, 2CH₃, d, J = 6.4 Hz), 0.94 (6H, 2CH₃, d, J = 6.4 Hz), 1.95 (2H, 2CH, octet, J = 6.4 Hz), 2.25 (3H, CH₃, s), 2.29 (6H, 2CH₃, s), 3.0-3.8 (2H, 2NH, s br, D₂O exchangeable), 4.0 (2H, 2CH-N, d J = 6.4 Hz), 5.12 (1H, CH, s), 6.36 (4H, Ar'H, d, J = 8.3 Hz), 6.73 (4H, Ar'H, d, J = 8.3 Hz), 6.95 (4H, Ar H, AB system, J = 7.8 Hz), 7.10 (8H, 2Ar H, AB system, J = 8.3 Hz). ¹³C NMR (CD₃Cl₃) δ 18.7 (CH₃), 19.6 (CH₃), 20.9 (CH₃), 21.9 (CH₃), 34.8 (CH), 54.7 (CH), 63.7 (CH-N), 112.9 (CH), 127.0 (CH), 128.6 (CH), 128.8 (CH), 129.1 (CH), 129.8 (CH), 133.3 (C), 136.1 (C), 139.6 (C), 142.4 (C), 145.8 (C) ppm. MS (EI, 70 eV) m/z 580 (M^+ , 13), 537 ($M - i$ -Pr, 80), 196 (100). HMRS calcd for C₄₂H₄₈N₂: 580.3817; found 580.3816.

N-Phenyl-{1-(*p*-bromophenyl)-*c*-hexhyl-methyl}amine (4k). Purification by flash column chromatography (hexane/EtOAc, 95:5) afforded **4k** (340 mg, 40%, Table 3, entry 3) as a reddish oil (first eluted product). ¹H NMR (CDCl₃) δ (ppm) 0.9-1.25 (5H, *c*-hexyl, m), 1.5-1.87 (6H, *c*-hexyl, m), 4.06 (1H, CH, d, J = 6.1 Hz), 6.47 (2H, Ar'H, d, J = 7.5 Hz), 6.63 (1H, Ar'H, t, J = 7.5 Hz), 7.06 (2H, Ar'H, t, J = 7.5 Hz), 7.17 (2H, Ar H, d, J = 8.1 Hz), 7.40 (2H, Ar H, d, J = 8.1 Hz). ¹³C NMR (CD₃Cl₃) δ 26.3 (CH₂), 29.3 (CH₂), 30.0 (CH₂), 44.6 (CH), 63.0 (CH-N), 113.3 (CH), 117.3 (CH), 127.4 (C-Br), 129.0 (CH), 129.1 (CH), 131.3 (CH), 141.5 (C), 147.2 (C) ppm. MS (EI, 70 eV) m/z 345-343 (M^+ , 20), 262-260 ($M - c$ -hexyl, 100). HMRS calcd for C₁₉H₂₂BrN: 343.0936; found 343.0937. The second eluted product was the **Triarylmethane derivative (5k)** (128 mg, 6% molar yield) as a green oil. ¹H NMR (CDCl₃) δ (ppm) 0.92-1.25 (10H, *c*-hexyl, m), 1.4-1.9 (12H, *c*-hexyl, m), 3.98 (2H, 2CH, d, J = 6.1 Hz), 5.11 (1H, CH, s), 6.32 (4H, Ar'H, d, J = 7.8 Hz), 6.70

(4H, Ar'H, d, J = 7.8 Hz), 6.87 (2H, Ar H, d, J = 8.4 Hz), 7.12 (4H, Ar H, d, J = 8.4 Hz), 7.29 (2H, Ar H, d, J = 8.4 Hz), 7.38 (4H, Ar H, d, J = 8.4 Hz). MS (CI) m/z 858-856-854-852 (M^+ , Br_3 pattern, 100). HMRS calcd for $C_{45}H_{47}N_2 Br_3$: 852.1289; found 852.1290.

N-[2-(3-Methyl)butane]-4-methoxyaniline (4m).^b Phenyldiazoniumfluoroborate (2.5 mmol) was added portionwise, over 2 h under stirring, to a CH_3COOH solution (15 mL), at 0°C, containing *p*-anisidine (2.5 mmol), *iso*-propyl iodide (7.5 mmol), acetaldehyde (10 mmol) and $TiCl_3$ (5 mmol, *ca.* 5 mL of a commercial aqueous solution). After stirring for additional 20 min, the reaction mixture was extracted with EtOAc (4x50 mL). The remaining work up was as for aromatic aldehydes. Purification of the crude residue by flash column chromatography (hexane/EtOAc, 9:1) afforded **4m** (240 mg, 50%) as a yellow oil. 1H NMR ($CDCl_3$) δ (ppm) 0.89 (3H, CH_3 , d, J = 6.9 Hz), 0.96 (3H, CH_3 , d, J = 6.9 Hz), 1.07 (3H, CH_3 , d, J = 6.5 Hz), 1.84 (1H, CH, m), 3.03 (1H, NH, br), 3.24 (1H, CH, dq, J = 7.0, 6.5 Hz), 3.74 (3H, OCH_3 , s), 6.55 (2H, Ar'H, d, J = 9.1 Hz), 6.76 (2H, Ar'H, d, J = 9.1 Hz). ^{13}C NMR ($CDCl_3$) δ 16.4 (CH_3), 17.1 (CH_3), 19.2 (CH_3), 32.0 (CH), 54.5 (CH), 55.7 (OCH_3), 114.5 (ArCH), 114.8 (ArCH), 142.0 (C), 151.7 (C) ppm. MS (EI, 70 eV) m/z 193 (M^+ , 10), 150 ($M - iso-Pr$, 100). Anal. calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found 74.52, 9.87, 7.28. ^bStauffer, S. R.; Sun, J.; Katzenellenbogen, B. S.; Katzenellenbogen, J. A.; *Bioorg. Med. Chem.* **2000**, 8, 1293-1316.